

EFFECTS OF TEMPERATURE AND SALINITY ON
ADSORPTION IN ALKALINE-SURFACTANT
FLOODING

CHE MOHD ARMAN CHE ISMAIL

UNIVERSITI TEKNOLOGI MALAYSIA

EFFECTS OF TEMPERATURE AND SALINITY ON ADSORPTION IN
ALKALINE-SURFACTANT FLOODING

CHE MOHD ARMAN CHE ISMAIL

A project report submitted in partial fulfilment of the
requirements for the award of the degree of
Master of Science (Petroleum Engineering)

Faculty of Petroleum & Renewable Energy Engineering
Universiti Teknologi Malaysia

JANUARY 2013

To my beloved mother and father,
To my lovely wife and kids,
and to all friends.
Thank you for your support.

ACKNOWLEDGEMENT

Alhamdulillah. First and foremost, I would like to give my gratitude to our beloved God for giving the opportunity for me to complete my research successfully. I also want to express my sincere appreciation to my supervisor, Associate Professor Dr. Mat Hussin bin Yunan for his guidance and assistance.

Never to forget, I would like to express my appreciation to all the technicians of Reservoir Engineering Lab in Faculty of Petroleum & Renewable Energy Engineering for their help and advices in order to finish my project.

Very special thanks go to my mother, my farther, my lovely wife and kids for their support and dedication.

Last but not least, thanks to all my family and friends who are involved directly or indirectly in preparing this report.

ABSTRACT

Alkaline-Surfactant flooding is one of the chemical flooding methods which are used to recover residual oil left after water flooding. By using a combination of alkaline and surfactant in the chemical formula, the interfacial tension (IFT) of oil/water is significantly reduced. However, surfactant adsorption on reservoir rocks is one of the major factors that may significantly reduce the effectiveness of an alkaline-surfactant flooding for oil recovery. The purpose of this study is to determine the effects of temperature and salinity on adsorption in an alkaline-surfactant flooding. In this study, parameter that was changed is the salinity of the brine (25000ppm, 30000ppm, 35000ppm, 40000ppm, 45000ppm). The optimum salinities as a given concentration will be was obtained of the temperature (30°C, 40°C, 50°C, 60°C, 70°C) on adsorption, surfactant IFT, residual oil recovery after water flood. The results of the study indicate that the residual oil recovery increases and surfactant adsorption will decreases as the temperature increases. The residual oil recovery decreases and surfactant adsorption will increases as brine salinity increases.

ABSTRAK

Banjiran surfaktan beralkali merupakan salah satu kaedah banjiran bahan kimia yang digunakan untuk memperolehi lebih minyak yang tertinggal selepas banjiran air. Dengan menggunakan kombinasi surfaktan dan alkali, regangan antara permukaan (IFT) minyak/air dapat dikurangkan. Walaubagaimanapun, penjerapan surfaktan didalam reserbor merupakan satu faktor utama yang mengurangkan keberkesanan banjiran surfaktan beralkali untuk perolehan minyak. Tujuan kajian ini adalah untuk mengenalpasti kesan suhu dan kemasinan air garam terhadap penjerapan didalam banjiran surfaktan beralkali. Dalam kajian ini, parameter yang di ubah ialah kemasinan air garam (25000ppm, 30000ppm, 35000ppm, 40000ppm, 45000ppm). Kemasinan untuk surfaktan beralkali yang optimum diperolehi daripada suhu (30°C, 40°C, 50°C, 60°C, 70°C) terhadap penjerapan, IFT surfaktan, peningkatan perolehan minyak selepas banjiran air. Keputusan kajian ini mendapati perolehan minyak baki meningkat dan penjerapan berkurang dengan peningkatan suhu. Perolehan minyak baki berkurang dan penjerapan meningkat dengan peningkatan kemasinan.

TABLE OF CONTENTS

| CHAPTER | TITLE | PAGE |
|----------------|--------------------------------|-------------|
| | DECLARATION | ii |
| | DEDICATION | iii |
| | ACKNOWLEDGEMENT | iv |
| | ABSTRACT | v |
| | ABSTRAK | vi |
| | TABLE OF CONTENTS | vii |
| | LIST OF TABLES | x |
| | LIST OF FIGURES | xii |
| | LIST OF APPENDICES | xiii |
| | LIST OF ABBREVIATION | xiv |
| 1 | INTRODUCTION | |
| | 1.1 Background of Research | 2 |
| | 1.2 Problem Statement | 3 |
| | 1.3 Objectives of The Research | 4 |
| | 1.4 Scope of The Study | 5 |

2 LITERATURE REVIEW

| | | |
|-------|---|----|
| 2.1 | Introduction to Chemical EOR | 6 |
| 2.2 | Alkali Flooding | 6 |
| 2.3 | Surfactant Flooding | 9 |
| 2.3.1 | Surfactant Classifications | 12 |
| 2.4 | Surfactant Used in the Research Study | 13 |
| 2.4.1 | Alpha Olefin Sulfonate | 14 |
| 2.5 | Interfacial Tension, IFT | 15 |
| 2.6 | Surfactant Retention | 18 |
| 2.6.1 | Surfactant Adsorption on Mineral Surface | 19 |
| 2.6.2 | Surfactant Precipitation | 20 |
| 2.6.3 | Phase Trapping | 21 |
| 2.7 | Effect of Salinity on Surfactant Adsorption | 22 |
| 2.8 | Effect of PH on Surfactant Adsorption | 25 |
| 2.9 | Minimizing Surfactant Adsorption | 27 |

3 METHODOLOGY

| | | |
|-------|-------------------------------------|----|
| 3.1 | Artificial Heterogeneous Core | 30 |
| 3.1.1 | Porosity Measurement | 31 |
| 3.1.2 | Permeability Measurement | 33 |
| 3.2 | Fluid System | 34 |
| 3.2.1 | Brine | 34 |
| 3.2.2 | Surfactant | 34 |
| 3.2.3 | Oil | 34 |
| 3.3 | Fluid Properties Determination | 35 |
| 3.3.1 | Specific Gravity Determination | 35 |
| 3.3.2 | Viscosity Determination | 35 |
| 3.3.3 | Oil API Gravity Determination | 36 |
| 3.3.4 | Density Determination | 36 |
| 3.4 | Interfacial Tension Measurement | 37 |
| 3.5 | Alkaline-Surfactant Flooding Method | 37 |

| | | |
|----------|--|----|
| 4 | RESULT AND DISCUSSION | |
| 4.1 | Core Properties Determination | 40 |
| 4.2 | Liquid Properties Determination | 41 |
| 4.3 | Surfactant Concentration Effect on Surface Tension | 44 |
| 4.4 | Effect of AOS Concentration on IFT in Various Salinities | 46 |
| 4.5 | Effect of Salinities Variation on Residual Oil Recovery | 48 |
| 4.6 | Effect of Salinities Variation on Surfactant Adsorption | 50 |
| 4.7 | Effect of Temperature on Residual Oil Recovery | 52 |
| 4.8 | Effect of Temperature on Surfactant Adsorption | 53 |
| 5 | CONCLUSIONS AND RECOMMENDATIONS | |
| 5.1 | Conclusions | 56 |
| 5.2 | Recommendations | 57 |
| | REFERENCES | 58 |
| | APPENDICES | |
| | APPENDIX A | 62 |
| | APPENDIX B | 63 |
| | APPENDIX C | 65 |
| | APPENDIX D | 70 |
| | APPENDIX E | 75 |
| | APPENDIX F | 80 |

LIST OF TABLES

| TABLE NO. | TITLE | PAGE |
|------------------|--|-------------|
| 2.1 | Factors influencing alkaline flooding | 8 |
| 2.2 | Composition of brine in malaysian oilfield | 25 |
| 2.3 | Surfactant Retention in Berea Cores | 26 |
| 2.4 | Specific Surface Areas of Some Reservoir Rocks and Clays | 28 |
| 4.1 | Core Properties | 41 |
| 4.2 | Oil properties | 42 |
| 4.3 | Brine properties | 44 |
| 4.4 | Result for AOS concentration effect on surface tension | 44 |
| 4.5 | Amount of surfactant adsorbed for different brine salinity. | 50 |
| 4.6 | Amount of surfactant adsorbed for different temperature. | 54 |

LIST OF FIGURES

| FIGURE NO. | TITLE | PAGE |
|-------------------|---|-------------|
| 2.1 | Alpha olefin sulfonate | 14 |
| 2.2 | Effect of acid number oils on the IFT and pH | 16 |
| 2.3 | IFT versus calcium ion concentration at pH 12 | 17 |
| 2.4 | Effect of different IFT on oil relative permeability curves | 18 |
| 2.5 | Typical phase behavior | 23 |
| 2.6 | Typical surfactant/oil/brine phase behavior | 24 |
| 3.1 | Artificial heterogeneous core | 31 |
| 3.2 | Vacuum Pump | 32 |

| | | |
|-----|--|----|
| 3.3 | Brookfield viscometer with a circulated temperature water bath | 36 |
| 3.4 | Easy Dyne Kruss tensionmeter | 37 |
| 3.5 | Core flooding setup | 39 |
| 4.1 | Critical micellar concentration determinations for AOS | 45 |
| 4.2 | IFT of AS solution at different concentration | 47 |
| 4.3 | Residual oil recovery after water flood in different salinities (NaCl) | 48 |
| 4.4 | Effect of brine salinities on residual oil recovery after water flood | 49 |
| 4.5 | Effect of brine salinities on surfactant adsorption after water flood | 51 |
| 4.6 | Residual oil recovery after water flood in different temperature | 52 |
| 4.7 | Effect of temperature on residual oil recovery after water flood | 53 |
| 4.8 | Effect of temperature on surfactant adsorption after water flood | 54 |

LIST OF APPENDICES

| APPENDIX | TITLE | PAGE |
|-----------------|---|-------------|
| A | Oil Specific Gravity Determination | 62 |
| B | Density Determination | 63 |
| C | Core Flooding Results (At Room Condition) | 65 |
| D | Cmc Value After Core Flood (At Room Condition) | 70 |
| E | Core Flooding Results (At Different Temperature) | 75 |
| F | Cmc Value After Core Flood (At Different Temperature) | 80 |

LIST OF ABBREVIATION

| | |
|---------------|---------------------------------|
| EOR | Enhanced Oil Recovery |
| IFT | Interfacial Tension |
| AOS | Alpha Olefin Sulfonate |
| IOR | Improved Oil Recovery |
| CMC | Critical Micellar Concentration |
| OH^- | Ion Hydroxide |
| PV | Pore Volume |
| NaOH | Sodium Hydroxide |
| Ppm | Parts per million |

LIST OF SYMBOLS

M – Mobility Ratio

k – Absolute Permeability, md

k_r – Relative Permeability, md

k_{rw} – Water Relative Permeability, md

k_{ro} – Oil Relative Permeability, md

μ – Viscosity, cp

λ – Mobility

v – Velocity, m/s

ρ – Density, kg/m³

H – Height, ft

L – Length, ft

N_c – Capillary Number

σ – Interfacial Tension, mN/m

ϕ – Porosity, %

V – Volume, ft³

Q – Flowrate, ft³/s

A – Area, ft²

ΔP – Pressure Change, psig

S_{wi} – Initial Water Saturation

CHAPTER 1

INTRODUCTION

Enhanced oil recovery (EOR) refers to the process of producing liquid hydrocarbon by using reservoir energy and pressure maintenance. On the average, conventional production methods will produce from a reservoir about 30% of the initial oil in place. The remaining oil, nearly 70% of the initial resource, is a large and attractive target for enhanced oil recovery methods (Terry et al., 1985).

These methods were developed with the objective of obtaining a larger production than that obtained just with the natural energy of the reservoir and they consist basically of the flooding of fluids seeking to move the oil outside of the pores of the rock. Thus, the injected fluid, called displacing fluid, should push the oil, called displaced fluid, outside of the rock and, at the same time, should occupy the left space.

Basically there are three categories in EOR which are thermal, miscible displacement and chemical process. Thermal processes where a hot invading face, such as steam or hot water or a combustible gas is injected in order to increase the temperature of the oil and gas in reservoir and facilitate their flow to the production wells by increasing the pressure and reducing the resistance to flow. Miscible

displacement process consists of injecting a miscible phase with the oil and gas into the reservoir in order to eliminate interfacial tension effect which uses inert gas. Finally a chemical flooding uses chemicals such as polymer, surfactant, alkaline to increase oil recovery. Alkali will react with crude oil to form in-situ surfactant and also increase pH. The polymer is used to improve the sweep efficiency of the invading fluid by changing the mobility ratio between the invading fluid and the displaced fluid. The surfactant seeks to reduce the interfacial tensions between the oil and the water, increasing the displacement efficiency (Schramm, 2000; Kwok et al., 1995). These types of chemicals can be combined together to complement each other in order to get the desired properties and functions.

Alkali-surfactant flooding is an established enhanced oil recovery technique in conventional oil reservoirs, whereby the injected chemical reduces the oil/water interfacial tension, leading to less trapping of oil ganglia.

1.1 Background of Research

The different combinations of chemical flooding (surfactant, alkali, and alkali-surfactant) are not a new technology. In 1956, Reisberg and Doscher proposed that a combination of performed surfactant and alkali could be injected along with water in order to improve recovery of oil. This recovery is generally attributed to the reduction in oil-water interfacial tension in the presence of surfactants. Surfactants are special molecules that are both hydrophobic and hydrophilic, thus the most stable configuration for them is at the interface between oil and water. By arranging themselves in this manner, surfactants can lead to dramatic reductions in the oil-water interfacial tension. It has been shown both experimentally and theoretically that when IFT has been reduced significantly, there is less capillary trapping of oil.

Alkali solutions are a special subset of surfactant flooding, whereby the injected alkali reacts with naturally occurring organic acids in the oil, leading to the generation of *in-situ* surfactants. In alkali flooding applications, the minimum oil/water IFT is often attained at very low concentrations of alkali. However, due to alkali losses from adsorption in the porous media, higher alkali concentrations often need to be injected. This leads to floods being performed at conditions that are not optimal for recovery, thus a mixture of alkali and surfactant is often injected in order to stabilize the flood at the optimum concentration for minimum IFT. This is the mechanism of alkali-surfactant flooding.

In chemical flooding, although it has been well documented that these floods do improve oil recovery compared to waterflooding, the mechanism responsible for the oil recovery is poorly understood. Suggested mechanisms include IFT reduction leading to less trapping of oil, rock wettability alteration, the formation of water/oil emulsions and the formation of oil/water emulsions. It is likely that all of these different parameters may play a role in different situations, however proper design of an AS flood requires an understanding of what should be happening as the injected AS solution mixes with the oil in the reservoir. Without this knowledge it becomes impossible to predict the response from an AS flood in a given oil reservoir.

1.2 Problem Statement

Based on previous research conducted by many researchers, dilute aqueous surfactant system will produce different properties in term of surfactant IFT and adsorption when different concentration of alkaline and surfactant used. Different concentration will result in different maximum oil recovery and surfactant adsorption. Salinity and temperature also affects the adsorption and value of oil recovery. Surfactant flooding process encounters problems due to loss of high cost surfactant in

the form of adsorption and retention in the reservoir rocks. This research is conducted by using a different salinity and temperature in order to find an optimum condition. New database regarding to the surfactant IFT, residual oil recovery and adsorption will be develop and can be applied to the field scale which have the same condition and parameters. The amount of oil recovered for field implementation can be roughly estimated by using the developed database.

1.3 Objectives of the Research

The objectives of this research are :-

1. To determine the optimum brine salinity that yield minimum surfactant adsorption.
2. To determine the effect of temperature on surfactant adsorption.
3. To get oil recovery from alkaline surfactant flooding process at various salinity and temperature in order to determine the optimum salinity and temperature.

1.4 Scope of Study

In this study, sand pack with two granule size of 125-220 μm and 450-600 μm used as porous media to represent heterogeneous reservoir. Sand pack model will be made from PVC pipe and designed with 45.7 cm of length and 3.2 cm of diameter. In this study, there are four types of fluid will be used. They are de-ionized water, brine, oil and surfactant. Several brine solution with different concentration will be prepared by dissolve sodium chloride (NaCl) into de-ionized water. While,

paraffin was used to represent oil instead of using crude oil because it's hard to get crude oil. Lastly, surfactant that used is Alpha Olefin Sulfonate (AOS). Alpha Olefin Sulfonate used in this study because it is a good surfactant, relatively stable, exhibit relatively low adsorption on reservoir rock and relatively cheap. Concentration of AOS that used is 0.05 %wt and fixed for all experiment. The controlling parameters in this study are brine salinity and temperature. The brine salinity will be test range between 25000 ppm to 45000 ppm. Meanwhile, the temperature is range between 30°C-70°C. All the experiment will be conducted at atmospheric pressure, 14.7 psig.

REFERENCES

- Al-Sahhaf T, Elkamel A, Ahmed AS, Khan AR (2005). *The Influence of Temperature, Pressure, Salinity, and Surfactant Concentration on the Interfacial Tension of the N-Octane–Water System*. Chem Eng Commun 192:667–684.
- Buckley, J.S. and Fan, T. (2007): *Crude Oil/Brine Interfacial tension. Paper 2005-01 Society of Petrophysicists and Well log analysts*. Vol. 48, no. 3, p. 175-185.
- Farouq Ali, S.M., Thomas, S. (1995). *How Do Surfactant and Caustic Floods Compare with Micellar Flooding?* University of Alberta. Paper PETSOC-95-79-P.
- Freer, E. M., Svitova, T. F., and Radke, C.J., (2003). *The Role of Interfacial Rheology in Reservoir Mixed Wettability*. Journal of Petroleum Science and Engineering, vol. 39, no. 1-2, 137–158.
- Gao, P., Towler, B. F., Li, Y., and Zhang, X. (2010). *Integrated Evaluation of Surfactant-Polymer Floods*, SPE 129590. SPE EOR Conference at Oil & Gas West Asia. 11-13 April, Muscat, Oman, 1-7.
- Glover, C.J., Puerto, M.C., Maerka, J.M., and Sandvik, E.L., “*Surfactant Phase Behavior and Retention in Porous Media*,” SPEJ, 183-193, June, 1979.

Goodlett, G. O., Honarpour, M. M., Chung, F. T., and Sarathi, P. S. (1986). *The Role of Screening and Laboratory Flow Studies in EOR Process Evaluation*, SPE 15172.

Green, D.W., and Willhite, G.P., *Enhanced Oil Recovery*, SPE Textbook Series Vol. 6, SPE inc., Richardson, TX, 1998.

Grigg, R.B. and Bai B., “*Sorption of Surfactant Used in CO₂ Flooding onto Five Minerals and Three Porous Media*,” SPE 93100, SPE International Symposium on Oilfield Chemistry, Woodlands, Texas, 2-4 February, 2005.

Healy, R.N., Reed, R.L. and Stenmark, D.K. (June 1976) *Multiphase Microemulsion Systems*, SPEJ, 147-160

Hill, H. J. and Lake, L. W., “*Cation Exchange in Chemical Flooding: Part3-Experimental*,” SPEJ, 18 (1978).

Hirasaki, G.J., and Zhang, D.L., “*Surface Chemistry of Oil Recovery from Fractured, Oil-Wet, Carbonate Formations*,” SPE 80988, presented at the SPE International Symposium on Oilfield Chemistry, Houston, TX, Feb.2003.

Holmberg K, Jönsson B (2003). *Surfactants and Polymers in Aqueous Solution*. John Wiley & Sons, England.

Jean Louis, (2002). *Laboratory of Formulations, Interfaces, Rheology and Processes. Surfactants Types and Uses: version 2*. (Booklet). Facultad De Ingenieria, Universidad De Los Andes.

Johnson, C.E. Jr.: “*Status of Caustic and Emulsion Methods*.” J. Pet. Tech. (Jan. 1976) 85-92.

Lake, L.W., *Enhanced Oil Recovery*, Prentice-Hall, Englewood Cliffs, NJ, 1989.

Lawson J.B. and Dilgren R.E, SPE Paper 6121, presented at the 51st Annual SPE Fall Technical Conference, New Orleans, (October 3-6, 1976).

Mathiassen, O. M. (2003). *CO₂ as Injection Gas for Enhanced Oil Recovery and Estimation of the Potential on the Norwegian Continental Shelf*. Norway : Norwegian University of Science and Technology.

Mayer, E.H. et al.: “*Alkaline Injection for Enhanced Oil Recovery - A Status Report*,” J. Pet. Tech. (Jan. 1983). 209-21.

Novosad, J. (1982). *Surfactant Retention in Berea Sandstone- Effects of Phase Behavior and Temperature*. Society of Petroleum Engineers Journal (Dec. 1982).

Ruckenstein E, Rao IV (1987) *Interfacial Tension of Oil–Brine Systems in the Presence of Surfactant and Cosurfactant*. J Colloid Interface Sci 117(1):104–119.

Santos FKG, Neto ELB, Moura MCPA, Dantas TNC, Neto AAD (2009). *Molecular Behavior of Ionic and Nonionic Surfactants in Saline Medium*. Colloids Surf, A Physicochem Eng Asp 333(1– 3):156–162.

Schramm L.L. (2000), *Fundamental & Application in Petroleum Industry* Cambridge England, Cambridge University Press.

Schramm, L.L. (1994). *Foams: Fundamentals and Application in the Petroleum Industry*. The American Chemical Society, Washington, DC. (Chapter 4)

Somasundaran, P., Celik, M., Goyal, A. and Manev, E. (1981). *The Role of Surfactant Precipitation and Redissolution in the Adsorption of Sulfonate on Minerals*. Society of Petroleum Engineers Journal (Apr. 1981). 233-239.

Taber, J. J., Martin, F. D., and Seright, R. S. (1997). *EOR Screening Criteria Revisited Part 2: Applications and Impact of Oil Prices*. SPE Reservoir Evaluation & Engineering. 12(3), 199-206.

Terry, R. E., J. K. Varma, et al. (1985). *The potential for enhanced oil recovery in the state of Wyoming*. Proceedings of the First Wyoming Enhanced Oil Recovery Symposium, University of Wyoming, Laramie.

Wesson, L.L., and Harwell, J.H., “*Surfactant Adsorption in Porous Media*”, *Surfactants: Fundamentals and Applications in the Petroleum Industry*, Schramm, L.L, ed., cambridge University Press, Cambridge, 2000.

Xu W, Ayirala SC, Rao DN (2005). *Measurement of Surfactant-Induced Interfacial Interactions at Reservoir Conditions*. SPE Journal SPE Paper 96021.

Ye Z, Zhang F, Han L, Luo P, Yang J, Chen H (2008). *The Effect of Temperature on the Interfacial Tension Between Crude Oil and Gemini Surfactant Solution*. Colloids Surf, A Physicochem Eng Asp 322(1–3):138–141.